Biotoners: Technology, Ecology and Markets

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Abstract

Biotoners represent a new class of electrostatic imaging powders that include a significant percentage of biobased materials. These include bioresins derived from crops, such as: corn, soy beans, sugar cane, sweet potatoes, or other renewable resources. In addition to a sustainable resin supply, biotoners offer other benefits, including the compostability1 of certain bioresins and their decomposition in the presence of water at elevated temperatures. This latter property is an important aid to the de-inking of office waste papers. Bioresin sources and the status of market development are provided in this commentary.

Introduction

The United States Department of Agriculture defines biobased products as those that are composed wholly or significantly of biological ingredients—renewable resources, such as plant, animal, marine or forestry materials. Note that this definition does not consider whether those products are compostable, decomposable or durable.

In a companion move, the USDA initiated a "Biopreferred" Program[2] to promote the increased purchase and use of biobased products. To the extent that the Biopreferred Program achieves its purpose the increased purchase of biobased products may reduce petroleum consumption, increase the use of renewable resources, better manage the carbon cycle, and contribute to reducing adverse environmental and health impacts. The Program is also expected to promote economic development, creating new jobs and providing new markets for farm commodities.

The USDA Biopreferred Program has two major initiatives: *Product Labeling* to increase consumer recognition of biobased products, and *Federal Procurement Preference* in which the USDA designates categories of biobased products that are afforded preference by Federal agencies when making purchasing decisions.

Bio-Based Polymers and Resins

The bio-based polymers and resins being used in the formulation of today's biotoners are derived from one of the following three sources:

1. Produced by glucose fermentation
2. Synthesized from biomonomers
3. Extracted from biomass

Glucose Fermentation.

In the first category are polyhydroxy alkanoates (PHA); polyhydroxy butyrates (PHB); marine algae; and, bacterial cellulose. The PHAs have found applications in film production and in disposable items, such as food, beverage and medical containers. Their high cost has been a limiting factor although some of these biopolymers have been used in combination with polylactides for imaging toners.

The PHBs are similar to the PHAs although a bit lower in cost and perhaps too brittle to be used alone in a toner formulation. However, when blended with nucleants and plasticizers, they can be used for some toner products.R&D efforts with marine algae are largely aimed at the development of biofuels, although some of this work will likely shift to bioresin development in the future.

From Biomonomers.

Polymers synthesized from bio-monomers, such as, polylactic acid (PLA) include the polylactides, and certain other polyesters, such as the polyisosorbide succinates (PIS), the polybutylene succinates (PBS), and the polyfuranics, e.g., polyetheylene furanoate[3] (PEF). These materials show promise in biotoner development.

From Biomass.

While field corn, soy beans and other crops are now the largest source of bio-based polymers, much activity is focused on replacing these starting materials with cellulosic biomass for toners and other bioplastic applications. The problem is that polymers derived from cellulosics are typically unstable.

It is believed that non-food, cellulosic biomass will ultimately become the preferred feedstock for all biopolymers. For toner applications, the challenge lies in satisfying the demanding thermal, physical and electrical properties unique to toner products. Currently, these characteristics can only be achieved by blending bio-based with some quantity of petro-based resins.

Generally speaking, starch alone cannot be used in toner formulations owing to its hygroscopic nature. It is being used, however, as an additive in starch/polymer blends for solid objects, such as bags, cutlery, plates and bottles.

In summary, the most common petro-based resins used in toner formulation are the styrene-acrylates, the polyesters, and the styrene-butadienes. Similarly, the most popular bio-based resins among toner formulators are the polylactides, polyhydroxy alkanoates, polyhydroxy butyrates, and isosorbide-based polyesters.

Benefits of Biotoner

Among the often cited benefits of biotoner are:

1. Reduces dependency on foreign oil
2. Can be biodegradable and compostable
3. Simplifies de-inking of office waste paper
4. Reduces overall CO_2 emissions in LCA[*]
5. Based upon a renewable resource
6. Uses lower cost bio-resins
7. Creates a growing consumer demand
8. Offers rechargers a leadership role

9. Satisfies the market's Green Initiative
10. Backed by USDA Biopreferred Program

*Life Cycle Assessment[4,5]

Biocontent

Despite the progress made over the past few years in developing biotoners that contain a significant percentage of biomass, there is no industry-accepted definition of what minimum level qualifies a product as a "biotoner." Nor, has there been universal agreement on how that percentage should be calculated.

The biocontent of a toner can be expressed as the percentage of renewable materials with respect to the total weight of *toner*. However, there is an ongoing dispute over this. Some express biocontent as the percentage of renewable materials with respect to the total weight of *carbon* in the toner. To others it is the percentage of bioresin with respect to the total weight of *resin*. There is no question that our industry must establish a universally-accepted definition of "biocontent." It is sorely needed to avoid the various interpretations and confusing definitions that are currently being bandied about.

In our view, the percent biocontent, or percent biomass should be measured with respect to the total weight of toner, not the resin component alone. Currently, for magnetic toners (used as developers) most commercially available biotoners are in the range of 20% to 30% biomass. Non-magnetic biotoners, can contain more than 30% biomass.

An excellent treatment of the issues of biocontent and biodegradability can be found in Dr. Ramani Narayan's tutorial on "Biobased and Biodegradable Plastics 101[6]."

Biocontent Analysis

The universally accepted method for determining the relative amount of biomass in toner, as opposed to petromass, is through radioactive carbon dating. Carbon has three isotopes: ^{12}C, ^{13}C and ^{14}C. Only ^{14}C is radioactive with a half-life of 5,730 years. That is the period of time it takes for a quantity of ^{14}C to undergo radioactive decay that will reduce its weight by half. The amount of residual ^{14}C in a carbonaceous sample reveals the age of that material. If it is zero, then that material is petro-mass.

We are aware of two laboratories[7,8] qualified to determine the biocontent of a substance. They are: Vincotte in Vilvoorde, Belgium, and Beta Analytic in Miami, Florida. Both use ASTM D6866 for this assessment[9].

Other Bioplastics

Fuji-Xerox has been actively promoting R&D efforts to replace the plastic parts in copy machines and printers with more environmentally friendly materials. One example is the introduction of biomass plastics using polymer alloy technology to achieve a homogeneous blend with petro-resins. The combination is unique as it affords a "carbon neutral" objective whereby the sum of CO_2 emitted by synthesis of the petro-based resin used in the bioplastic is offset by the CO_2 absorbed in the photo-synthesis process involved in the growth of the biomass (corn, soy beans, etc.) used to produce the bioresin. In other words, it's a zero sums game in which the CO_2 absorbed by the growing plant from which the bioresin is derived is equal to the CO_2 emitted by the process used to synthesize the petro-resin.

Canon is reported to be working on bio/petro plastic blends for printer cartridges and frames. They have reportedly developed a PLA/ABS blend.

Toner Formulation Criteria

One of the issues impeding development of new bioresins for toner formulation is the relatively limited understanding of toner properties among many polymer chemists. In our view, toner is one of the most sophisticated plastic products with respect to its processing characteristics and imaging performance. Following is a partial list of criteria.

- ✓ Biocontent
- ✓ Bioresin particle size and shape
- ✓ Brittleness or frangibility
- ✓ Compatibility with petro-based resins
- ✓ Compatibility with wax, pigment, CCA
- ✓ Gel content or degree of cross-linking
- ✓ Glass transition temperature
- ✓ Environmental stability (HH, LL, LH, HL)
- ✓ Frangibility, or jet mill throughput
- ✓ Impurities
- ✓ Melt and softening temperature
- ✓ Melt index
- ✓ Moisture content
- ✓ Pigment dispersion capability

Development Status of Biotoner Resins

Resin grades are evolutionary at this stage. Properties are being optimized by polymer chemists. Biopolymers and bio-monomers have vast potential for applications with conventional mechanical toners (CMT) and chemical process toners (CPT) for both monochrome and color print making.

Most monochrome office applications are being addressed at present, but are high-speed toners for commercial printing a distant dream? The answer depends upon how fast consumers adopt biotoners in general and how fast resin makers can learn to modify existing biopolymers to enable 100% bioresin content in imaging toners.

Chemical process biotoners are at a very early stage of development as existing CPT producers are pre-occupied with the perfection of conventional color imaging toners. Nevertheless, Purac is offering polylactic acid (PLA) monomer for this purpose and recently announced plans for a10,000 metric ton (mt) per year PLA plant in Thailand[10].

Markets

Currently, the global demand for all toners, mono-chrome and color, magnetic and non-magnetic is believed to be in the range of 200,000 mt per year. Of this amount, color toners account for perhaps 15% or 20%. Our estimate for monochrome biotoner consumption in 2011 would be under 1,500 mt, or less than 1% of the total volume sold. This volume is shared primarily by Mitsubishi Kagaku (Future Graphics), SoyPrint, Ricoh, Konica-Minolta and others.

With strong promotion and consumer education, we expect a compound annual growth rate in sales volume of 15% to 20% over the coming 5 years. This would bring the annual global volume in 2016 to between 3,200 and 3,700 mt.

The *Green Initiative* is an important driver in the demand for biotoner. *Green* thinking is already widespread throughout the world of printing. Soy-based printing inks have taken an important position in conventional offset, flexographic and gravure printing operations. Commercial printing is a growth market in many countries outside of the United States.

Industry analysts report[11] the demand for biotoners is strongest in Europe, followed by a rising interest in the United States. But, enthusiasm for biotoners is relatively weak in China, India, Indonesia, Japan and other Asian countries.

There are four main barriers to market growth for biotoners: First, the product is available from just a few sources; second, available biotoners have been formulated to suit a limited number of printer models; third, many consumers are reluctant to replace traditional toners with those based upon a grown and harvested plant, because it would reduce the available supply of food for humans; and fourth, there is objection, especially in Europe, to the use of bioresins derived from genetically modified (GM) corn or soy feedstocks.

This last barrier concerns government restrictions, specifically in Europe, on the use of GM crops. For centuries, corn has been a staple food among nations in the Western Hemisphere. In Europe, however, it was long considered to be "animal food" unfit for human consumption.

Clearly, the feedstock for bioresin is not *food* corn; it is *field* corn. The difference is that *food* corn is raised to feed humans; *field* corn is raised to feed animals.

In America, the agricultural industry, supported by the USDA, has spent millions on genetic engineering to develop better strains of crops that are more drought resistant, more insect resistant and faster growing. GM corn exists primarily to feed farm animals and to produce biofuels such as ethanol and bioplastics. Monsanto's Roundup™ glyphosate herbicide is one of the most effective weed killers in farming.

Monsanto's Roundup Ready™ corn, soy beans and alfalfa enable farmers to spray their fields liberally for no-till weed control. The savings in farm labor, tractor fuel and the addition of about $16 per acre to a soybean grower's bottom line provide increased profits over traditional systems.

Unfortunately, some European countries are either considering restrictions or have already placed them on the use of biotoner based upon resin derived from GM crops. The rationale is a most controversial issue, namely, the unintended consequence of hard-to-kill "superweeds." Here, the danger is similar to the dilemma of antibiotic overuse in humans. Over time, the weeds develop increased resistance to the herbicide.

All things considered, we believe the power of the *Green Initiative*, as it gains strength in nations worldwide, will overcome these barriers.

References

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[2] See www.biopreferred.gov

[3] "Aventium Raises About $43 Million for Furanics-Based Next Generation Polyester,"West Virginia Manufacturers Association, June 9, 2011.

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[11] V. R. Sankaran and A. S. Diamond, Biotoners: Benefits, Barriers and Breakthroughs, Recharge Asia, **86**:16-22 June 2011.

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